1 **MIXED MATRIX MEMBRANE WITH SUPER WATER WASHED SILICA**
2 **CONTAINING MOLECULAR SIEVES AND METHODS FOR MAKING AND**
3 **USING THE SAME**

4

5 <u>TECHNICAL FIELD</u>

6

7 This invention relates to mixed matrix membranes and methods for making

8 the same, and more particularly, to those membranes having silica containing

9 molecular sieves, such as zeolites, which are used to separate components of

10 a gaseous mixture.

11

12 <u>BACKGROUND OF THE INVENTION</u>

13

14 Mixed matrix membranes have proven to be effective in separating gas

15 components contained within a gaseous mixture. The mixed matrix

16 membranes typically contain molecular sieves which are embedded within

17 polymeric organic materials. Mixed matrix membranes exhibit the unusual

18 effect that the selectivity of the combined molecular sieves and organic

19 polymer are higher than that of the organic polymer alone.

20

21 An example of such a mixed matrix membrane is found in

22 U.S. Pat. No. 5,127,925 to Kulprathipanji et al. Another exemplary patent is

23 U.S. Pat. No. 4,925,459 to Rojey et al. which describes the use of molecular

24 sieves supported by an organic polymer to create a membrane which is useful

25 for the separation of gas components. In both patents, membranes utilize

26 zeolites as a molecular sieve. Zeolites are silica containing molecular sieves

27 which have a particularly highly ordered crystalline structure often with

28 desirable pore sizes and shapes conducive for fluid separations.

29

30 An example of the preparation of a zeolite, i.e., SSZ-13, is taught in

31 U.S. Pat. No. 4,544,538 to Zones. Another example of preparation of a

32 zeolite, SSZ-62, is described in U.S. Patent Application 2003/0069449 to

1 Zones et al. The disclosures found in each of these patent documents are
2 hereby incorporated by reference in their entireties.
3
4 The manufacture of zeolites used in mixed matrix membranes may include
5 the step of lowering the concentration of alkali metals in the zeolite by
6 converting the zeolite to a hydrogen form. This is conventionally done by ion
7 exchange, generally with ammonium cations. After ion-exchange, the zeolite
8 is calcined to decompose the ammonium cations, thereby converting the
9 zeolite from an ammonium form to the hydrogen form.
10
11 While this method of treating zeolite particles prior to their incorporation into
12 an organic polymer may benefit membrane selectivity and/or permeability to a
13 degree, there is a need to discover improved zeolites and methods of treating
14 those zeolites to achieve even better separation performance. While
15 improved performance could also be achieved by increasing the zeolite
16 content in a membrane, technical difficulties in membrane preparation
17 (e.g., fiber spinning) and membrane strength can limit the upper percentage of
18 zeolites that can be added. Accordingly, finding a way to get more effective
19 use from a given content of zeolite would have distinct advantages. Higher
20 selectivity will mean less loss of potentially valuable retentate to a permeate
21 stream of fluids being separated. Higher permeability will reduce the required
22 membrane area, thereby reducing investment cost.
23
24 In converting zeolite to the hydrogen form, it has been found that if ammonium
25 cations are not completely removed, the residual cations can partially restrict
26 diffusion of a gas, e.g., CO_2, through pores in the zeolite, reducing membrane
27 permeability and selectivity. Second, complete removal of the ammonium
28 cations is difficult, requiring calcination at temperatures above 400°C,
29 generally above 450°C or even 500°C. This high temperature calcination can
30 degrade certain properties of zeolites. While not wishing to be bound by
31 theory, this could potentially include dehydroxylation of silanol groups at the
32 surface of the zeolite, where these groups are necessary for a high degree of
33 attachment of silating agents. These silating agents can provide a bonding

1   link between the zeolite and the membrane polymer phase. Without this link,

2   gas may bypass the zeolite particles, diminishing separation selectivity. Other

3   linking methods via surface silanol groups are also possible, such as through

4   reactive groups in the polymer itself. Again, a decrease of these silanol

5   groups would negatively impact that linking.

6

7   Another factor which could decrease zeolite effectiveness is residual

8   amorphous siliceous material at the surface of the zeolite which could block

9   surface sites and/or diminish diffusion of gases through the zeolite. Calcining

10   the zeolite to remove the organic template prior to implementing procedures

11   designed to remove amorphous material could anchor the amorphous

12   material at the zeolite surface, making it difficult to remove and leading to

13   poorer membrane performance. Blocking of surface sites could also lead to a

14   diminishing of the surface charge (Zeta-potential) of the zeolite, making the

15   zeolite particles easier to agglomerate during membrane formation which

16   could also lead to poorer membrane performance.

17

18   Thus, there is a need to produce mixed matrix membranes with higher

19   permeability and selectivity for a given loading of molecular sieves. The

20   present invention addresses this need by overcoming some of the above

21   described shortcomings of conventional mixed matrix membranes and in their

22   manufacture.

23

24   SUMMARY OF THE INVENTION

25

26   The present invention provides a method for preparing silica containing

27   molecular sieves which may be mixed with an organic polymer to create a

28   mixed matrix membrane. Further, this invention includes a method of making

29   such a mixed matrix membrane and the membrane itself.

30

31   The method for preparing silica containing molecular sieves comprises super

32   water washing silica containing molecular sieves to produce water washed

33   molecular sieves which are substantially free of surface remnants. Super

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1   water washing ideally also lowers the concentration of alkali metals in the

2   molecular sieves. The water washed sieves are sufficiently free of surface

3   remnants such that when the water washed sieves are subjected to a

4   Sieve Wash Conductivity Test, a wash filtrate is produced having a

5   conductivity of less than 110 micro mhos/cm, more preferably less than

6   80 micro mhos/cm, even more preferably less than 50 micro mhos/cm, and

7   most preferably less than 30 micro mhos/cm. It is believed that super

8   washing the sieves to this degree will enhance, compared to conventional

9   preparation techniques, the ability of the molecular sieves to bond with an

10   organic material to form a highly selective and permeable mixed matrix

11   membrane. The Sieve Wash Conductivity Test will be described in further

12   detail below.

13

14   The silica containing molecular sieves used in this invention are selected for

15   their pore and crystal structure such that when the molecular sieves are used

16   in a mixed matrix membrane, the membrane will exhibit superior permeability

17   and selectivity performance. It is believed this superior performance is, in

18   part, due to the super water washing of the molecular sieves, during

19   preparation of the membranes.

20

21   The method for preparing silica containing molecular sieves comprises super

22   water washing silica containing molecular sieves to produce water washed

23   molecular sieves which are substantially free of surface remnants. Super

24   water washing ideally also lowers the concentration of alkali metals in the

25   molecular sieves.

26

27   The water washed sieves are sufficiently free of surface remnants such that

28   when the water washed sieves are subjected to a Sieve Wash Conductivity

29   Test, a wash filtrate is produced having a conductivity of less than

30   110 micro mhos/cm, more preferably less than 80 micro mhos/cm, even more

31   preferably less than 50 micro mhos/cm, and most preferably less than

32   30 micro mhos/cm. After the super water washing, the sieve particles are

33   thereafter dried and calcined at a temperature high enough to decompose any

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1 organic template, typically 450°C to 700°C. It is believed that super washing

2 the sieves to this degree will enhance, compared to conventional preparation

3 techniques, the ability of the molecular sieves to bond with an organic material

4 to form a highly selective and permeable mixed matrix membrane.

5

6 Mixed matrix membranes made in accordance with this invention may be

7 used in a process for separating component gases of a gas mixture. The

8 mixed matrix membranes comprise silica containing molecular sieves

9 dispersed in a continuous phase of a polymer. The sieves have been

10 sufficiently super water washed prior to being incorporated into the continuous

11 phase to be substantially free of surface remnants, such that when subjected

12 to a Sieve Wash Conductivity Test, a wash filtrate is produced having a

13 conductivity of less than 110 micro mhos/cm, more preferably less than

14 80 micro mhos/cm, even more preferably less than 50 micro mhos/cm, and

15 most preferably less than 30 micro mhos/cm. The gas mixture contacts one

16 side of the membrane to cause the component gases to selectively permeate

17 through the membrane. This allows a permeate gas composition enriched in

18 concentration of at least one component gas to be removed from the opposite

19 side of the membrane.

20

21 It is an object of this invention to produce a mixed matrix membrane which

22 utilizes silica containing molecular sieves which have been super water

23 washed prior to incorporation into an organic polymer carrier.

24

25 It is another object to super water wash, rather than use ammonium ion

26 exchange, to lower the concentration of alkali metals in silica containing

27 molecular sieves and to remove surface remnants such that pores of the

28 molecular sieves are more resistant to blocking and the surfaces of the

29 molecular sieves are more susceptible to attachment to a polymer phase

30 when making a mixed matrix membrane.

31

32 Still another object is to increase the permeability and selectivity of a mixed

33 matrix membrane made with a given loading of silica containing molecular

1 sieves by employing super water washing rather than ammonium ion

2 exchange to lower the concentration of alkali metals in the sieves and to

3 remove surface remnants prior to calcining of the sieves.

4

5 <u>BRIEF DESCRIPTION OF THE DRAWINGS</u>

6

7 These and other objects, features and advantages of the present invention

8 will become better understood with regard to the following description,

9 pending claims and accompanying drawings where:

10

11 FIG. 1 is a graph of CO_2/N_2 selectivity vs. CO_2 permeability for PVAc-MMC

12 films without molecular sieves and with ~15% (wt. %) H-SSZ-62 loading; and

13

14 FIG. 2 is a graph of O_2/N_2 selectivity vs. O_2 permeability for PVAc films

15 without molecular sieves and PVAc-MMC films with ~15% (wt. %) H-SSZ-62

16 loading.

17

18 <u>BEST MODE(S) FOR CARRYING OUT THE INVENTION</u>

19

20 A.   INTRODUCTION

21

22 The present invention includes a method for making a mixed matrix

23 membrane with super washed silica containing molecular sieves. First, the

24 preparation and processing of the silica containing molecular sieves, including

25 the super water washing of the molecular sieves, will be described. Next, the

26 method of making mixed matrix membranes containing super washed silica

27 containing molecular sieves will be discussed. Finally, specific examples of

28 making silica containing molecular sieves, mixed matrix membranes including

29 silica containing molecular sieves, and results of permeability and selectivity

30 tests using the mixed matrix membranes for gas component separation will be

31 presented.

1 B.   PREPARATION AND PROCESSING OF SILICA CONTAINING
2   MOLECULAR SIEVES
3
4 The silica containing molecular sieves to be used in this invention are
5 selected for their pore and crystal characteristics such that when used in a
6 mixed matrix membrane, the membrane will exhibit superior permeability and
7 separation performance. It is believed this superior performance is, in part,
8 also due to the super water washing of the sieves during preparation of the
9 membranes. The super washing preferably replaces, or at least augments,
10 conventional steps of ion exchanging used to lower alkali metal
11 concentrations in silica containing molecular sieves. Also, by super water
12 washing remnants from the sieves, pores remain open and surface charges
13 are also believed to remain such that the sieves are less likely to agglomerate
14 during membrane preparation. This surface preparation may lead to better
15 bonding between the sieves and organic polymers thereby enhancing the
16 selectivity and performance of mixed matrix membranes made using the
17 super water washed sieves.
18   ″
19   1.   PREPARATION OF SSZ-62
20
21 The most preferred silica containing molecular sieve to be used with the
22 present invention is SSZ-62 and may be prepared as follows. A
23 N,N,N-trimethyl-1-adamantammonium cation is used as a crystallization
24 template or structure directing agent ("SDA"). In general, SSZ-62 is prepared
25 by contacting an aluminum hydroxide gel dried to about 50 wt. % Al_2O_3 with a
26 slight alkalinity and the ability to absorb CO_2 and solubilize rapidly in water,
27 precipitated silica with a water content of about 5 to 15 wt. %, and a
28 templating agent comprising a N,N,N-trimethyl-1-adamantammonium cation.
29 SSZ-62 is prepared from a reaction mixture having the composition shown in
30 Table 1 below. Silicon- and aluminum-containing reactants are expressed as
31 SiO_2 and Al_2O_3, respectively.

Table 1　　Reaction Mixture

	Typical	Preferred
SiO_2/Al_2O_3	20 - 50	25 - 40
OH^-/SiO_2	0.15 - 0.40	0.25 - 0.40
Q/SiO_2	0.10 – 0.35	0.18 - 0.22
$M_{2/n}/SiO_2$	0.05 - 0.20	0.12 - 0.18
H_2O/SiO_2	10 - 25	12 – 20

where Q is the SDA, M is alkali metal or alkaline earth metal, and n is the valence of M.

In practice, SSZ-62 is prepared by a process comprising:

a.　preparing an aqueous solution containing an aluminum hydroxide gel dried to about 50 wt. % Al_2O_3 with a slight alkalinity and the ability to absorb CO_2 and solubilize rapidly in water, precipitated silica with a water content of about 5 to 15 wt. % and a N,N,N-trimethyl-1-adamantammonium cation having an anionic counterion which is not detrimental to the formation of SSZ-62;

b.　maintaining the aqueous solution under conditions sufficient to form crystals of SSZ-62; and

c.　recovering the crystals of SSZ-62.

The source of silicon is precipitated silica with a water content of about 5 to 15 wt. %. An example of such a material is HiSil 233 available from PPG Industries, Inc.
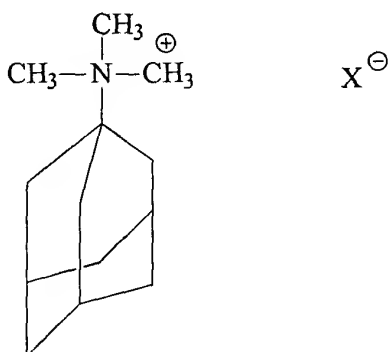
1   The source of aluminum is an aluminum hydroxide gel dried to about

2   50 wt. % Al_2O_3. The gel has slight alkalinity and is able to absorb CO_2. It is

3   rapidly soluble in water. The aluminum hydroxide has a particle density of

4   less than about 1.0 g/cm^3, preferably less than about 0.9 g/cm^3, more

5   preferably less than about 0.8 g/cm^3, and most preferably in the range of

6   about 0.1 g/cm^3 to about 0.8 g/cm^3. An example of such a material is

7   Reheis F-2000 available from Reheis Chemical Co.

8

9   The aluminum hydroxide, as added to the reaction mixture, further has an

10   average particle size of less than about 40 microns, preferably less than about

11   25 microns, more preferably less than about 15 microns, still more preferably

12   less than about 10 microns, and most preferably within the range of about

13   0.1 to 10 microns, with preferably less than about 25% of the particulates

14   having a particle size outside the range of about 0.1 to 40 microns. In a more

15   preferred embodiment, less than about 25%, even more preferably less than

16   10%, of the particles have a particle size outside the range of about

17   0.1 to about 25 microns.

18

19   The aluminum hydroxide gel has a low alkali level before it is added to the

20   reaction mixture. The gel contains less than about 0.12 wt. % and preferably

21   less than 0.10 wt. % alkali. It is most preferred that the gel have an alkali

22   content in the range of about 0.01 wt. % to about 0.10 wt. % where alkali may

23   be one or more of the Group IA elements.

24

25   Typically, an alkali metal hydroxide and/or an alkaline earth metal hydroxide,

26   such as the hydroxide of sodium, potassium, lithium, cesium, rubidium,

27   calcium, and magnesium, is used in the reaction mixture; however, this

28   component can be omitted so long as the equivalent basicity is maintained.

29   The templating agent may be used to provide hydroxide ion. Thus, it may be

30   beneficial to ion exchange, for example, the halide for hydroxide ion, thereby

31   reducing or eliminating the alkali metal hydroxide quantity required. The alkali

32   metal cation or alkaline earth cation may be part of the as-synthesized

1 crystalline oxide material, in order to balance valence electron charges

2 therein.

3

4 The SDA used to prepare SSZ-62 is a N,N,N-trimethyl-1-adamantammonium

5 cation having the following structure:

6

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{|}{N}}-CH_3 \quad \oplus \qquad\qquad X^{\ominus}$$

7

8 The anion (X⁻) associated with the cation may be any anion which is not

9 detrimental to the formation of the zeolite. Representative anions include

10 halogen, e.g., fluoride, chloride, bromide and iodide, hydroxide, acetate,

11 sulfate, tetrafluoroborate, carboxylate, and the like. Hydroxide is the most

12 preferred anion.

13

14 The reaction mixture is maintained at an elevated temperature until the

15 crystals of the SSZ-62 zeolite are formed. The hydrothermal crystallization is

16 usually conducted under autogenous pressure, at a temperature between

17 100°C and 200°C, preferably between 135°C and 160°C. The crystallization

18 period is typically greater than 1 day and preferably from about

19 3 days to about 20 days.

20

21 Preferably, the zeolite is prepared using mild stirring or agitation. During the

22 hydrothermal crystallization step, the SSZ-62 crystals can be allowed to

23 nucleate spontaneously from the reaction mixture. The use of SSZ-62

24 crystals as seed material can be advantageous in decreasing the time

25 necessary for complete crystallization to occur. In addition, seeding can lead

26 to an increased purity of the product obtained by promoting the nucleation

1   and/or formation of SSZ-62 over any undesired phases. When used as

2   seeds, SSZ-62 crystals are added in an amount between 0.1 and 10% of the

3   weight of silica used in the reaction mixture.

4

5   For the purpose of this specification, a Sieve Wash Conductivity Test is

6   conducted as follows. Ten (10) grams of the water washed molecular sieves

7   (on a volatiles-free basis) are mixed with 250mL of deionized water and kept

8   at 95°C in a closed Teflon bottle for 18 hours. Alkali ions, surface remnants,

9   and other residuals may be released from the sieve particles into the

10 deionized water at a relatively slow rate at room temperature. Accordingly, to

11 insure that the sieve particles are sufficiently free of surface remnants and/or

12 alkali ion, etc., this Sieve Wash Conductivity Test provides that the mixture of

13 deionized water and sieve particles be kept at 95°C in a closed Teflon bottle

14 for 18 hours, to allow ions and particles to go into solution prior to conductivity

15 being tested.

16

17 The mixture is then cooled to room temperature and filtered to produce a

18 wash filtrate. The conductivity of the wash filtrate is measured using a

19 conductivity meter (e.g., Cole-Parmer Model 1484-20). If the sieves have

20 been sufficiently super water washed, then the conductivity of the wash filtrate

21 should be below the aforementioned prescribed conductivity levels, i.e., below

22 110, 80, 50 or 30 micro mhos/cm.

23

24 The zeolites, after recovery and filtration, are preferably washed with water

25 until the conductivity, measured at room temperature with a conductivity

26 meter, falls below 110 micro mhos/cm, more preferably below

27 80 micro mhos/cm, even more preferably below 50 micro mhos/cm, and most

28 preferably below 30 micro mhos/cm. The super water washing of the

29 molecular sieves may take place in a single wash step. Alternatively, the

30 super water washing may be done batchwise in several repeated cycles.

31 Although not preferred, it is possible to wash the zeolites with a basic solution

32 with a pH of at least 9, and more preferably at least 11 prior to beginning the

33 super water washing process.

1   The zeolite is then dried and calcined at a temperature high enough to

2   decompose any organic template, typically 450°C to 700°C, preferably

3   500°C to 650°C. It is preferred that the super water washing take place prior

4   to the calcining step. This allows impurities to be washed away which

5   otherwise might remain affixed to the molecular sieve due to the calcining

6   step. The crystals are water-washed and then dried, e.g., at 90°C to 150°C

7   for 8 to 24 hours, to obtain the as-synthesized SSZ-62 zeolite crystals. The

8   drying step can be performed at atmospheric pressure or under vacuum.

9

10   SSZ-62 as prepared has a mole ratio of silicon oxide to aluminum oxide of

11   greater than 10. SSZ-62 can also be made with a mole ratio of silicon oxide

12   to aluminum oxide of at least 30. The crystallite size of SSZ-62, as

13   determined by TEM, is less than 0.5 micron, and is preferably less than

14   0.1 micron.

15

16   The zeolite particle size can be reduced after synthesis such as by high shear

17   wet milling. Prior to membrane formation, the zeolite may be silanated, either

18   during wet milling or separately. It is believed that silanation permits improved

19   bonding between the zeolite outer surface and the polymer. Suitable silane

20   compounds include 3-aminopropyldimethylethoxysilane and

21   3-isocyanopropyldimethylchlorosilane. Silanation can be carried out, for

22   example, by mixing the zeolite in an ethanol/water mixture containing the

23   silane compound for a period of time (a few minutes up to a few hours), then

24   recovering the treated zeolite and washing with ethanol to remove excess

25   silane. For more details on the silanation, U.S. Pat. No. 6,508,860 may be

26   reviewed, the teachings of which are hereby incorporated by reference in its

27   entirety.

1   2.   PREPARATION OF SSZ-13

2

3   Another preferred silica containing molecular sieve which may be used in this

4   invention is SSZ-13 zeolite. SSZ-13 zeolites can be suitably prepared from

5   an aqueous solution containing sources of an alkali metal oxide, an organic

6   compound, an oxide of aluminum or gallium, or mixture of the two, and an

7   oxide of silicon or germanium, or mixture of the two. The reaction mixture

8   should have a composition in terms of mole ratios of oxides falling within the

9   following ranges:

10

11   _____

12   **Table 2   Reaction Mixture**

13

14		Broad	Preferred
15	YO_2/W_2O_3	5-350	12-200
16	M_2O/W_2O_3	0.5-20	1-17
17	R_2O/W_2O_3	0.5-40	5-25
18	MCl/W_2O_3	20-200	50-150

19   _____

20

21   wherein R is as disclosed below, Y is silicon, germanium or both, and

22   W is aluminum, gallium or both. M is an alkali metal, preferably sodium or

23   potassium. Typically, an alkali metal hydroxide or alkali metal halide is used

24   in the reaction mixture; however, these components can be omitted so long as

25   the equivalent basicity is maintained. The organic compound can provide

26   hydroxide ion. The OH^-/YO_2 mole ratio to produce SSZ-13 having

27   silica:alumina mole ratios of less than about 20:1 is above about 0.95 and is

28   preferably in the range of 0.95 to 1.10. To prepare high silica content SSZ-13,

29   the OH^-/YO_2 mole ratio is below about 0.95.

30

31   The organic component of the crystallization mixture is typically a bicyclo

32   heteroatom compound. The heteroatom is preferably nitrogen. The preferred

33   organic species are derivatives of either 1-adamantamine, 3-quinuclidinol, or

-13-

1   2-exo-aminonorbornane. The quaternary lower alkylammonium cation
2   derivatives of these compounds are especially preferred. Methyl and other
3   lower alkyl derivatives can be made using standard synthetic procedures.
4
5   The reaction mixture is prepared using standard zeolitic preparation
6   techniques. Typical sources of aluminum oxide for the reaction mixture
7   include aluminates, alumina, and aluminum compounds such as $AlCl_3$ and
8   $Al_2(SO_4)_3$. Typical sources of silicon oxide include silicates, silica hydrogel,
9   silicic acid, colloidal silica, tetraalkyl orthosilicates, and silica hydroxides.
10 Gallium and germanium can be added in forms corresponding to their
11 aluminum and silicon counterparts. Salts, particularly alkali metal halides
12 such as sodium chloride, can be added to or formed in the reaction mixture.
13 They are disclosed in the literature as facilitating the crystallization of zeolites
14 while preventing silica occlusion in the lattice.
15
16 The reaction mixture is maintained at an elevated temperature until the
17 crystals of the zeolite are formed. The temperatures during the hydrothermal
18 crystallization step are typically maintained from about 100°C to about 235°C,
19 preferably from about 120°C to about 200°C, and most preferably from about
20 130°C to about 165°C. The crystallization period is typically greater than
21 3 days and preferably from about 7 days to about 50 days. The hydrothermal
22 crystallization is conducted under pressure and usually in an autoclave so that
23 the reaction mixture is subject to autogenous pressure. The reaction mixture
24 can be stirred during crystallization. Once the zeolite crystals have formed,
25 the solid product is separated from the reaction mixture by standard
26 mechanical separation techniques such as filtration.
27
28 The zeolites, after recovery and filtration, are washed with water until the
29 conductivity, measured at room temperature with a conductivity meter, falls
30 below 110 micro mhos/cm, more preferably below 80 micro mhos/cm, even
31 more preferably below 50 micro mhos/cm, and most preferably below

1 30 micro mhos/cm. The zeolite is then dried and calcined at a temperature

2 high enough to decompose any organic template, typically 450°C to 700°C,

3 preferably 500°C to 650°C.

4

5 The crystals are water-washed and then dried, e.g., at 90°C to 150°C for

6 8 to 24 hours, to obtain the as-synthesized, SSZ-13 zeolite crystals. The

7 drying step can be performed at atmospheric or subatmospheric pressures.

8

9 During the hydrothermal crystallization step, the SSZ-13 crystals can be

10 allowed to nucleate spontaneously from the reaction mixture. The reaction

11 mixture can also be seeded with SSZ-13 crystals both to direct and accelerate

12 the crystallization, as well as to minimize the formation of undesired

13 aluminosilicate contaminants. If the reaction mixture is seeded with SSZ-13

14 crystals, the concentration of the organic compound can be greatly reduced or

15 eliminated, but it is preferred to have some organic compound present, e.g.,

16 an alcohol.

17

18 The zeolite particle size can be reduced after synthesis such as by high shear

19 wet milling. Prior to membrane formation, the zeolite may be silanated, either

20 during wet milling or separately. It is believed that silanation permits improved

21 bonding between the zeolite outer surface and the polymer. Suitable silane

22 compounds include 3-aminopropyldimethylethoxysilane and

23 3-isocyanopropyldimethylchlorosilane. Silanation can be carried out, for

24 example, by mixing the zeolite in an ethanol/water mixture containing the

25 silane compound for a period of time (a few minutes up to a few hours), then

26 recovering the treated zeolite and washing with ethanol to remove excess

27 silane.

28

29   3.   OTHER MOLECULAR SIEVE CANDIDATES

30

31 Mixed matrix membranes utilizing molecular sieves containing significant

32 quantities of silica are believed to benefit from the super water washing of the

1 present invention. Along with zeolites, other molecular sieves which should

2 benefit include silicoaluminophosphates (SAPOs).

3

4 Molecular sieves, both natural and synthetic, are well known and are

5 described in the following, all of which are incorporated by reference in their

6 entireties: W.M. Meier, D.H. Olson and Ch. Baerlocher in

7 *Atlas of Zeolite Structure Types*, Elsevier, 4th Edition, London (1996),

8 *Molecular Sieves, Principles of Synthesis and Identification* by

9 R. Szostak (Van Nostrand Reinhold, 1989); and *Zeolite Molecular Sieves*, by

10 D. Breck, John Wiley and Sons, 1973.

11

12 In all cases, a super washing step, instead of a cursory washing step, will be

13 used to remove excessive residual remnants from the freshly formed and

14 filtered zeolite crystals. This super washing step should significantly reduce

15 amounts of harmful residual remnants remaining on the zeolite crystals.

16 When these zeolite crystals are super washed and a Sieve Wash Conductivity

17 Test is performed, the wash filtrate will have conductivity of less than

18 110 micro mhos/cm, more preferably below 80 micro mhos/cm, even more

19 preferably below 50 micro mhos/cm, and most preferably below

20 30 micro mhos/cm. The zeolite is then dried and preferably calcined at a

21 temperature high enough to decompose any organic template, typically

22 450°C to 700°C, and more preferably 500°C to 650°C. The molecular sieves

23 are also ideally silanated as described above.

24

25 C.   MAKING MIXED MATRIX MEMBRANE

26

27   1.   POLYMER SELECTION

28

29 An appropriately selected polymer can be used which permits passage of the

30 desired gases to be separated, for example, carbon dioxide and methane.

31 Preferably, the polymer permits one or more of the desired gases to permeate

32 through the polymer at different diffusion rates than other components, such

33 that one of the individual gases, for example, carbon dioxide, diffuses at a

faster rate through the polymer. In a preferred embodiment, the rate at which carbon dioxide passes through the polymer is at least 10 times faster than the rate at which methane passes through the polymer.

For use in making mixed matrix membranes for separating CO_2 and CH_4, the most preferred polymers include Ultem® 1000, Matrimid® 5218, 6FDA/BPDA-DAM, 6FDA-6FpDA, and 6FDA-IPDA (all polyimides). Ultem® 1000 is a polyetherimide and is commercially available from General Electric Plastics. Matrimid® 5218 is made by Ciba. 6FDA/BPDA-DAM and 6FDA-IPDA are available from DuPont and are described in U.S. Pat. No. 5,234,471.

Examples of suitable polymers include substituted or unsubstituted polymers and may be selected from polysulfones; poly(styrenes), including styrene-containing copolymers such as acrylonitrilestyrene copolymers, styrene-butadiene copolymers and styrene-vinylbenzylhalide copolymers; polycarbonates; cellulosic polymers, such as cellulose acetate-butyrate, cellulose propionate, ethyl cellulose, methyl cellulose, nitrocellulose, etc.; polyamides and polyimides, including aryl polyamides and aryl polyimides; polyethers; polyetherimides; polyetherketones; poly(arylene oxides) such as poly(phenylene oxide) and poly(xylene oxide); poly(esteramide-diisocyanate); polyurethanes; polyesters (including polyarylates), such as poly(ethylene terephthalate), poly(alkyl methacrylates), poly(acrylates), poly(phenylene terephthalate), etc.; polypyrrolones; polysulfides; polymers from monomers having alpha-olefinic unsaturation other than mentioned above such as poly (ethylene), poly(propylene), poly(butene-1), poly(4-methyl pentene-1), polyvinyls, e.g., poly(vinyl chloride), poly(vinyl fluoride), poly(vinylidene chloride), poly(vinylidene fluoride), poly(vinyl alcohol), poly(vinyl esters) such as poly(vinyl acetate) and poly(vinyl propionate), poly(vinyl pyridines), poly(vinyl pyrrolidones), poly(vinyl ethers), poly(vinyl ketones), poly(vinyl aldehydes) such as poly(vinyl formal) and poly(vinyl butyral), poly(vinyl amides), poly(vinyl amines), poly(vinyl urethanes), poly(vinyl ureas), poly(vinyl phosphates), and poly(vinyl sulfates); polyallyls; poly(benzobenzimidazole);

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1 polyhydrazides; polyoxadiazoles; polytriazoles; poly (benzimidazole);

2 polycarbodiimides; polyphosphazines; etc., and interpolymers, including block

3 interpolymers containing repeating units from the above such as terpolymers

4 of acrylonitrile-vinyl bromide-sodium salt of para-sulfophenylmethallyl ethers;

5 and grafts and blends containing any of the foregoing. Typical substituents

6 providing substituted polymers include halogens such as fluorine, chlorine and

7 bromine; hydroxyl groups; lower alkyl groups; lower alkoxy groups;

8 monocyclic aryl; lower acyl groups and the like.

9

10 It is preferred that the membranes exhibit a carbon dioxide/methane

11 selectivity of at least about 5, more preferably at least about 10, and most

12 preferably at least about 30. Preferably, the polymer is a rigid, glassy polymer

13 as opposed to a rubbery polymer or a flexible glassy polymer. Glassy

14 polymers are differentiated from rubbery polymers by the rate of segmental

15 movement of polymer chains. Polymers in the glassy state do not have the

16 rapid molecular motions that permit rubbery polymers their liquid-like nature

17 and their ability to adjust segmental configurations rapidly over large

18 distances (>0.5 nm). Glassy polymers exist in a non-equilibrium state with

19 entangled molecular chains with immobile molecular backbones in frozen

20 conformations. The glass transition temperature (Tg) is the dividing point

21 between the rubbery or glassy state. Above the Tg, the polymer exists in the

22 rubbery state; below the Tg, the polymer exists in the glassy state. Generally,

23 glassy polymers provide a selective environment for gas diffusion and are

24 favored for gas separation applications. Rigid, glassy polymers describe

25 polymers with rigid polymer chain backbones that have limited intramolecular

26 rotational mobility and are often characterized by having high glass transition

27 temperatures (Tg>150°C).

28

29 In rigid, glassy polymers, the diffusion coefficient tends to dominate, and

30 glassy membranes tend to be selective in favor of small, low-boiling

31 molecules. The preferred membranes are made from rigid, glassy polymer

32 materials that will pass carbon dioxide (and nitrogen) preferentially over

33 methane and other light hydrocarbons. Such polymers are well known in the

1   art and are described, for example, in U.S. Pat. No. 4,230,463 to Monsanto
2   and U.S. Pat. No. 3,567,632 to DuPont. Suitable membrane materials include
3   polyimides, polysulfones and cellulosic polymers.

5   2.   METHODS OF FORMING THE MIXED MATRIX MEMBRANE

7   The mixed matrix membranes are typically formed by casting a homogeneous
8   slurry containing particles and a desired polymer, as described above. The
9   slurry can be mixed, for example, using homogenizers and/or ultrasound to
10 maximize the dispersion of the particles in the polymer or polymer solution.
11 The casting process is preferably performed by three steps:

13   a.   pouring the solution onto a flat, horizontal surface
14   (preferably glass surface),

16   b.   slowly and virtually completely evaporating the solvent from the
17   solution to form a solid membrane film, and

19   c.   drying the membrane film.

21 To control the membrane thickness and area, the solution is preferably
22 poured into a metal ring mold. Slow evaporation of the solvent is preferably
23 effected by covering the area and restricting the flux of the evaporating
24 solvent. Generally, evaporation takes about 12 hours to complete, but can
25 take longer depending on the solvent used. The solid membrane film is
26 preferably removed from the flat surface and placed in a vacuum oven to dry.
27 The temperature of the vacuum oven is preferably set from about
28 50°C to about 110°C (or about 50°C above the normal boiling point of the
29 solvent) to remove remaining solvent and to anneal the final mixed matrix
30 membrane.

32 The final, dried mixed matrix membrane can be further annealed above its
33 glass transition temperature Tg. The Tg of the mixed matrix membrane can

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1 be determined by any suitable method (e.g., differential scanning calorimetry).

2 The mixed matrix film can be secured on a flat surface and placed in a high

3 temperature vacuum oven. The pressure in the vacuum oven

4 (e.g., Thermcraft® furnace tube) is preferably between about

5 0.01mm Hg to about 0.10mm Hg. Preferably, the system is evacuated until

6 the pressure is 0.05mm Hg or lower. A heating protocol is programmed so

7 that the temperature reaches the Tg of the mixed matrix membrane preferably

8 in about 2 to about 3 hours. The temperature is then raised to preferably

9 about 10°C to about 30°C, but most preferably about 20°C, above the Tg and

10 maintained at that temperature for about 30 minutes to about two hours. After

11 the heating cycle is complete, the mixed matrix membrane is allowed to cool

12 to ambient temperature under vacuum.

13

14 The resulting mixed matrix membrane is an effective membrane material for

15 separation of one or more gaseous components from gaseous mixtures

16 including the desired component(s) and other components. In a non-limiting

17 example of use, the resulting membrane has the ability to separate carbon

18 dioxide from methane, is permeable to these substances, and has adequate

19 strength, heat resistance, durability and solvent resistance to be used in

20 commercial purifications. While not wishing to be bound to a particular theory,

21 the molecular sieves are believed to improve the performance of the mixed

22 matrix membrane by including selective holes/pores with a size that permits

23 carbon dioxide to pass through, but either not permitting methane to pass

24 through, or permitting it to pass through at a significantly slower rate. The

25 molecular sieves should have higher selectivity for the desired gas separation

26 than the original polymer to enhance the performance of the mixed matrix

27 membrane. For the desired gas separation in the mixed matrix membrane, it

28 is preferred that the steady-state permeability of the faster permeating gas

29 component in the molecular sieves be at least equal to that of the faster

30 permeating gas in the original polymer matrix phase.

31

32 The membranes can be used in any convenient form such as sheets, tubes or

33 hollow fibers. Hollow fibers can be preferred, since they provide a relatively

1 large membrane area per unit volume. Sheets can be used to fabricate spiral
2 wound modules familiar to those skilled in the art.
3
4 For flat-sheet membranes, the thickness of the mixed matrix selective layer is
5 between about 0.001 and 0.005 inches, preferably about 0.002 inches. In
6 asymmetric hollow fiber form, the thickness of the mixed matrix selective skin
7 layer is preferably about 1,000 Angstroms to about 5,000 Angstroms. The
8 loading of particles in the continuous polymer phase is between about
9 10% and 60%, preferably about 20% to 50% by volume.
10
11   3.   METHODS OF FORMING HOLLOW FIBERS
12
13 Hollow fibers can be formed, for example, by extruding a polymer/molecular
14 sieve mixture through a tubular capillary nozzle with a core fluid used for the
15 purpose of retaining the hollow fiber shape. These fibers typically have the
16 diameter of a human hair and offer the advantage of maximizing the surface
17 area per unit volume. Industrial hollow fiber membrane modules typically
18 contain hundreds of thousands of individual hollow fibers.
19
20 Specifically, to maximize productivity, the hollow fibers typically include an
21 ultrathin (<2,000 Angstroms) "skin" layer on a porous support. Gas separation
22 is accomplished through this selective "skin". This outer "skin" layer may be
23 supported on the same polymer to form an integrally skinned asymmetric
24 hollow fiber membrane. The most advanced membranes have an asymmetric
25 sheath with the selective skin supported on an inexpensive porous core layer
26 (different polymer) to form a composite hollow fiber membrane. This type of
27 device is described in U.S. Pat. No. 5,085,676, the contents of which are
28 hereby incorporated by reference. In the present invention, the selective
29 outer skin or sheath is comprised of the molecular sieve membrane including
30 the molecular sieves dispersed in a continuous phase polymer. The
31 supportive core preferably does not contain sieves, but may.

Hollow fibers can be employed in bundled arrays potted at either end to form tube sheets and fitted into a pressure vessel thereby isolating the insides of the tubes from the outsides of the tubes. Devices of this type are known in the art. Preferably, the direction of flow in a hollow fiber element will be counter-current rather than co-current or even transverse. Such counter-current flow can be achieved by wrapping the hollow fiber bundle in a spiral wrap of flow-impeding material. This spiral wrap extends from a central mandrel at the center of the bundle and spirals outward to the outer periphery of the bundle. The spiral wrap contains holes along the top and bottom ends, whereby gas entering the bundle for tube side flow at one end is partitioned by passage through the holes and forced to flow parallel to the hollow fiber down the channel created by the spiral wrap. This flow direction is counter-current to the direction of flow inside the hollow fiber. At the bottom of the channels, gas re-emerges from the hollow fiber bundle through the holes at the opposite end of the spiral wrap and is directed out of the module.

D.   MIXED MATRIX MEMBRANE ENHANCEMENT TEST

A test can be prepared to verify that the molecular sieves have been properly and successfully made to produce mixed matrix membranes with greatly enhanced permeation properties. This test involves preparation of a sample mixed matrix membrane film using a test polymer and a specified loading of molecular sieves, and comparing the CO_2/CH_4 permeation and selectivity versus a membrane film of the same test polymer without added sieves. The CO_2/CH_4 permeation selectivity is determined by taking the ratio of the permeability of CO_2 over that of CH_4. The permeability of a gas penetrant i is a pressure-and thickness-normalized flux of the component through the membrane and is defined by the expression:

$$P_i = \frac{N_i \cdot \ell}{\Delta p_i}$$

where P_i is permeability of component i, ℓ is thickness of the membrane layer, N_i is component i's flux (volumetric flow rate per unit membrane area) through the membrane, and Δp_i is the partial pressure driving force of component i (partial pressure difference between the upstream to the downstream). Permeability is often expressed in the customary unit of Barrer (1 Barrer = 10^{-10} cm^3 (STP) ·cm/cm^2·s·cm Hg). Permeability measurements can be made using a manometric, or constant volume, method. The apparatus for performing permeation measurements in films is described in O'Brien et al., *J. Membrane Sci.*, 29, 229 (1986) and Costello et al., *Ind. Eng. Chem. Res.*, 31, 2708 (1992), the contents of which are hereby incorporated by reference.
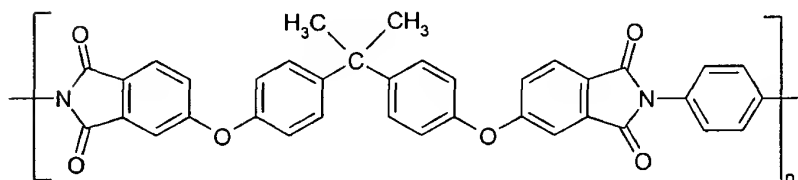
In the CO_2/CH_4 Mixed Matrix Enhancement Test, permeation tests of pure gases of CO_2 and CH_4 are performed on the mixed matrix membrane. The mixed matrix membrane film is separately tested with each gas using an upstream pressure of about 50 psig and a vacuum downstream. A temperature of about 35°C is maintained inside the permeation system. Similar permeation tests of pure gases of CO_2 and CH_4 are performed on a prepared membrane film of the same test polymer without added sieves. To confirm that the molecular sieves particles have been properly prepared by the methods described herein, the mixed matrix membrane film should exhibit a CO_2/CH_4 selectivity enhancement in the CO_2/CH_4 Mixed Matrix Enhancement Test of 10% or more, preferably 15% or more, over the CO_2/CH_4 selectivity of the pure test polymer membrane alone.

1 The method for forming the sample mixed matrix membrane for use in the
2 Enhancement Test is as follows:
3
4   1.   The sieve is first silanated according to the following procedure:
5
6   a.   Prepare a 200mL of 95:5 (by volume) solution of
7   isopropyl alcohol (ACS certified grade or better) and
8   DI water.
9
10   b.   Add the 4 grams silane coupling agent
11   (3-aminopropyldimethylethoxysilane, APDMES is the
12   standard) to the sieve (5 grams, based on dry weight) in a
13   plastic container. Next, add the IPA solution prepared in
14   step a.
15
16   c.   Sonicate the mixture with an ultrasonic horn for
17   30 minutes in five minute intervals (five minutes
18   sonication followed by five minutes of resting).
19
20   d.   Filter the solution with a high pressure (~120psi) nitrogen
21   filtration setup (Pall Gelman #4280) using
22   0.2µm PTFE filter paper.
23
24   e.   Once the filtration is complete, add 100mL fresh IPA and
25   sonicate the mixture above the paper, being careful not to
26   contact the filter paper with the sonicator tip. This breaks
27   up the cake so that excess APDMES is evenly washed
28   off the surface. Repeat this procedure with two additional
29   aliquots of IPA.

f.   Set the sieve aside until ready to incorporate into a film.

2.   For the purpose of the Enhancement Test, the polymer to be used for the matrix phase is Ultem® 1000 (GE Plastics). Its chemical structure is shown below.

Dry the Ultem® 1000 and silanated zeolite in a vacuum oven at 120°C.

3.   Prepare a 25 wt. % Ultem® 1000 solution in $CHCl_3$ and set aside until sieve priming is complete.

4.   Disperse 1.5 grams of the silanated sieve and 0.2 grams Ultem® 1000 in 200mL NMP(N-methyl pyrolidone) via sonication for two minutes in a round bottom flask. Maintain this mixture at 140°C (oil bath) for four hours under a dry nitrogen purge, stirring constantly.

5.   Filter the solution with 0.2μm filter paper, wash the resulting cake three times with pure NMP, then dry overnight at 135°C in a vacuum oven.

6.   Disperse a portion of the sieve for two minutes via sonication in enough $CHCl_3$ so that the polymer-sieve-solvent system has 15% solids.

7. Add enough of the Ultem-CHCl$_3$ solution prepared in step 3 to give a 15:85 sieve:polymer mixture, then allow the solution to gently mix on a roller until it appears homogeneous. Remove the solution from the roller ten minutes before casting to allow any entrapped bubbles to escape.

8. Cast the solution on Teflon coated glass in a glove bag with a 10 mil casting knife with Al tape added to the bottom to increase the clearance to 16 mil. Cover with a funnel to control evaporation rate.

9. Remove the film carefully by pulling it off the surface, and dry it in an aluminum foil envelope in the vacuum oven at 180°C for seven days.

10. To perform the Enhancement Test, permeability measurements of the flat mixed matrix membrane films are required. The measurements can be made using a manometric, or constant volume, method. A sample film area from final mixed matrix film is masked with adhesive aluminum masks having a circular, pre-cut, exposed area for permeation through the membrane. The masked membrane can be placed in a permeation cell and the permeation system. Both the upstream and downstream sections of the permeation system are evacuated for about 24 hours to 48 hours to remove ("degas") any gases or vapors sorbed into the membrane. Permeation tests of the membrane can be performed by pressurizing the upstream side with the desired gas at the desired pressure, in this test 50 psig with a temperature of 35°C. The permeation rate can be measured from the pressure rise of a pressure transducer and using the known downstream (permeate) volume. Following the permeation testing of a given gas, both the upstream and

1   downstream sections are evacuated for at least 12 hours before

2   permeation testing of the next gas.

3

4   With the above procedure, the CO_2 and CH_4 permeabilities are measured for

5   the test mixed matrix membrane and the pure test polymer (Ultem® 1000).

6   The CO_2/CH_4 selectivity of the mixed matrix membrane is compared to the

7   CO_2/CH_4 selectivity of the pure test polymer (Ultem® 1000) alone. A CO_2/CH_4

8   selectivity enhancement of 10% or more should be observed in the mixed

9   matrix membrane film.

10

11   E.   SEPARATION SYSTEMS INCLUDING THE MEMBRANES

12

13   The membranes may take any form known in the art, for example, hollow

14   fibers, tubular shapes, and other membrane shapes. Some other membrane

15   shapes include spiral wound, pleated, flat sheet, or polygonal tubes. Multiple

16   hollow fiber membrane tubes can be preferred for their relatively large fluid

17   contact area. The contact area may be further increased by adding additional

18   tubes or tube contours. Contact may also be increased by altering the

19   gaseous flow by increasing fluid turbulence or swirling.

20

21   The preferred glassy materials that provide good gas selectivity, for example,

22   carbon dioxide/methane selectivity, tend to have relatively low permeabilities.

23   A preferred form for the membranes is, therefore, integrally skinned or

24   composite asymmetric hollow fibers, which can provide both a very thin

25   selective skin layer and a high packing density, to facilitate use of large

26   membrane areas. Hollow tubes can also be used.

27

28   Sheets can be used to fabricate a flat stack permeator that includes a

29   multitude of membrane layers alternately separated by feed-retentate spacers

30   and permeate spacers. The layers can be glued along their edges to define

31   separate feed-retentate zones and permeate zones. Devices of this type are

32   described in U.S. Pat. No. 5,104,532, the contents of which are hereby

33   incorporated by reference.

1 The membranes can be included in a separation system that includes an
2 outer perforated shell surrounding one or more inner tubes that contain the
3 mixed matrix membranes. The shell and the inner tubes can be surrounded
4 with packing to isolate a contaminant collection zone.
5
6 In one mode of operation, a gaseous mixture enters the separation system via
7 a containment collection zone through the perforations in the outer perforated
8 shell. The gaseous mixture passes upward through the inner tubes. As the
9 gaseous mixture passes through the inner tubes, one or more components of
10 the mixture permeate out of the inner tubes through the selective membrane
11 and enter the containment collection zone.
12
13 The membranes can be included in a cartridge and used for permeating
14 contaminants from a gaseous mixture. The contaminants can permeate out
15 through the membrane, while the desired components continue out the top of
16 the membrane. The membranes may be stacked within a perforated tube to
17 form the inner tubes or may be interconnected to form a self-supporting tube.
18
19 Each one of the stacked membrane elements may be designed to permeate
20 one or more components of the gaseous mixture. For example, one
21 membrane may be designed for removing carbon dioxide, a second for
22 removing hydrogen sulfide, and a third for removing nitrogen. The
23 membranes may be stacked in different arrangements to remove various
24 components from the gaseous mixture in different orders.
25
26 Different components may be removed into a single contaminant collection
27 zone and disposed of together, or they may be removed into different zones.
28 The membranes may be arranged in series or parallel configurations or in
29 combinations thereof depending on the particular application. The gaseous
30 mixture can flow through the membrane(s) following an inside-out flow path
31 where the mixture flows into the inside of the tube(s) of the membranes and
32 the components which are removed permeate out through the tube.

1 Alternatively, the gaseous mixture can flow through the membrane following
2 an outside-in flow path.
3
4 In order to prevent or reduce possibly damaging contact between liquid or
5 particulate contaminates and the membranes, the flowing gaseous mixture
6 may be caused to rotate or swirl within an outer tube. This rotation may be
7 achieved in any known manner, for example, using one or more spiral
8 deflectors. A vent may also be provided for removing and/or sampling
9 components removed from the gaseous mixture.
10
11 The membranes are preferably durable, resistant to high temperatures, and
12 resistant to exposure to liquids. The materials may be coated, ideally with a
13 polymer, to help prevent fouling and improve durability. Examples of suitable
14 polymers include those described in U.S. Pat. Nos. 5,288,304 and 4,728,345,
15 the contents of which are hereby incorporated by reference. Barrier materials
16 may also be used as a pre-filter for removing particulates and other
17 contaminants which may damage the membranes.
18
19 Mixed matrix membranes made in accordance with this invention may be
20 used in a process for separating component gases of a gas mixture. The
21 mixed matrix membranes comprise silica containing molecular sieves
22 dispersed in a continuous phase of a polymer. The sieves have been
23 sufficiently super water washed prior to being incorporated into the continuous
24 phase to be substantially free of surface remnants, such that when subjected
25 to a Sieve Wash Conductivity Test, a wash filtrate is produced having a
26 conductivity of less than 110 mhos/cm, more preferably less than
27 80 mhos/cm, even more preferably less than 50 mhos/cm, and most ·
28 preferably less than 30 mhos/cm. The gas mixture contacts one side of the
29 membrane to cause the component gases to selectively permeate the
30 membrane. This allows a permeate gas composition enriched in
31 concentration of at least one component gas to be removed from the opposite
32 side of the membrane.

1 F.   EXAMPLES

2

3   EXAMPLE 1:   Preparation of H-SSZ-62

4

5 H-SSZ-62 was prepared according to the following procedure:

6

7 To a mixture of 1,836.2 grams of 0.64M N,N,N-trimethyl-1-

8 adamantammonium hydroxide and of 3,336 grams deionized H_2O were added

9 46.2 grams of sodium hydroxide solids (98%). This was stirred until the

10 NaOH was dissolved. Then 28.35 grams of Reheis F-2000 alumina were

11 added with continued stirring for another 30 minutes. Next, 342.2 grams of

12 Cabosil M-5 were added with stirring. The mix was loaded into a stirred

13 5 gallon autoclave and run at 160°C for four days. At the end of run, the

14 reaction mixture had a final pH of 12.22. The mix was then filtered. The wet

15 filter cake was then heated overnight at 90°C in 1.5 liters of a 0.1N NaOH

16 solution to remove excess silica that did not get incorporated into the zeolite.

17 (This corresponds to a pH of greater than 12.) The zeolite was separated by

18 centrifugation, and then heated overnight at 90°C in deionized water.

19

20 The zeolite was separated by centrifugation, and then washed repeatedly in

21 deionized water until the wash water had a conductivity of

22 110 micro mhos/cm, measured at room temperature with a

23 Cole-Parmer conductivity meter (Model 1484-20). The zeolite was further

24 washed until the conductivity of the wash water was 30 micro mhos/cm or

25 less. During washing, the Na content of the zeolite was reduced from

26 0.46 wt. % in the starting material to 0.36 wt. % in the final product. The

27 zeolite was then dried overnight at 90°C. Particle size by SEM was about

28 0.1 to 0.5 microns. The dried zeolite was then calcined in air at 593°C for

29 five hours. Micropore analysis showed the zeolite had a micropore volume of

30 0.3 cc/g. The silica/alumina molar ratio of the zeolite by ICP was 29. The

31 zeolite was then silanated with APDMES using 0.2% APDMES in

32 isopropanol/water (95:5 V/V) and dried at 135°C overnight. The zeolite was

33 used to prepare an Ultem® 1000 mixed matrix membrane with

1   15 wt. % H-SSZ-62 zeolite content using the methods described above for the

2   Mixed Matrix Membrane Enhancement Test.

3

4   EXAMPLE 2:   Permeation Testing

5

6   Permeability measurements were made using a manometric, or constant

7   volume, method. The permeation tests were conducted in accordance with

8   permeation test procedures described above in Section D.

9

10   The permeation properties of the neat Ultem® 1000 were determined using a

11   gas mixture containing 10% CO_2 and 90% CH_4. The upstream side of the

12   neat Ultem® 1000 film was exposed to this gas mixture at a pressure of

13   50 psia. The downstream side of the neat Ultem® 1000 was maintained at

14   vacuum, resulting in a differential pressure driving force of 50 psia across the

15   film. With the permeation system maintained at a constant temperature of

16   35°C, the permeation rate of gases through the membrane was measured

17   with a pressure-rise method and the composition of the permeate gas was

18   analyzed with gas chromatography (HP 6880). Results are shown in Table 3

19   with the individual gas permeabilities.

20

21   ————————————————————————————

22   **Table 3   "Neat" Ultem® 1000 Membrane**

23

24   Gas Component   Permeability $(10^{-10}$ cm^3 (STP) •cm/cm^2•s•cm Hg)

25   CH_4 0.038

26   CO_2 1.49

27   ————————————————————————————

28

29   From the permeability values in Table 3, the permeability ratios (selectivity) of

30   the neat Ultem® 1000 membrane film for CO_2/CH_4 was 39.2.

31

32   A section from the mixed matrix film (15 wt. % H-SSZ-62) in Example 1 was

33   used to measure the permeabilities and separation factor at 50 psia and

1 35°C for 10% CO_2/90% CH_4. Results are shown in Table 4 with the individual

2 gas permeabilities.

3

4 _____

5 **Table 4   Ultem® 1000 With Super Water Washed Sieves Membrane**

6

7 <u>Gas Component</u>   <u>Permeability (10^{-10} cm^3 (STP) •cm/cm^2•s•cm Hg)</u>

8 CH_4 0.055

9 CO_2 2.81

10 _____

11

12 From the permeability values in Table 4, the permeability ratios (selectivity) of

13 the mixed matrix membrane for CO_2/CH_4 was 51.1. Both the CO_2/CH_4

14 selectivity and CO_2 permeability of the Ultem® 1000-H-SSZ-62 mixed matrix

15 membrane, using super water washing, were enhanced over those measured

16 for the neat Ultem® 1000 film.

17

18   *COMPARATIVE EXAMPLE A*

19

20 H-SSZ-62 zeolite particles were prepared which were calcined prior to the

21 super water washing step. All the other preparation steps were the same as

22 those described in Example 1 including silanation. The particles were dried in

23 a vacuum oven for 24 hours at 100°C. A mixed matrix membrane was

24 prepared, again using Ultem® 1000 as the polymer matrix phase. As before,

25 this mixed matrix membrane film contained 15 wt. % H-SSZ-62 particles.

26

27 Unlike the mixed matrix film prepared in Example 1, the resulting mixed matrix

28 film using these H-SSZ-62 particles had a markedly different morphology and

29 physical appearance, containing numerous, large agglomerates that resulted

30 in a texture similar to that of sandpaper, whereas the mixed matrix film

31 employing the desired super washed H-SSZ-62 particles (Example 1) was

32 physically smooth and free of agglomerates. A section from the film was used

1   in a permeation testing cell to measure the permeabilities and separation

2   factor at 50 psia and 35°C for 10% CO_2/90% CH_4.

3

4   The permeation rate was not measurable because of its high rate. Further,

5   gas chromatography analysis of the permeate stream indicated no

6   compositional difference from that of the feed mixture.

7

8   *COMPARATIVE EXAMPLE B*

9

10 H-SSZ-62 was prepared according to U.S. Patent Application 2003/0069449

11 to Zones et al, using ion-exchange to lower metal alkali content as taught in

12 that application. Conventional water washing of the H-SSZ-62 was performed

13 before calcination. Again, these sieves were silanated with APDMES. The

14 sieves were used to prepare a mixed matrix membrane containing

15 15% zeolite, with PVAc as the polymer. The O_2/N_2 selectivity at 50 psia and

16 35°C was 6.5. In comparison, a membrane made using the super water

17 washed sieves of Example 1, also containing 5% H-SSZ-62, had an O_2/N_2

18 selectivity at 50 psia and 35°C of 7.0.

19

20   *COMPARATIVE EXAMPLE C*

21

22 The H-SSZ-62 of Comparative Example B, i.e., silanated sieves made without

23 using super water washing, was used to make a 15% zeolite mixed matrix

24 membrane with Ultem$^®$ 1000 as the polymer. The membrane was tested for

25 both O_2/N_2 and CO_2/CH_4 separation. No selectivity enhancement was found

26 at 50 psia and 35°C over that of the neat polymer.

27

28   EXAMPLE 3:   Permeation Testing - PVAc – 30 micro mhos/cm

29

30 The H-SSZ-62 zeolite of Example 1, which was silanated, was used to

31 prepare a mixed matrix membrane film using polyvinylacetate (PVAc), with a

32 15% zeolite loading. Samples of the film were tested for both CO_2/N_2 and

33 O_2/N_2 permeation, using the pure gases at 50 psi and 35°C. Results are

1   shown, respectively, in FIGS. 1 and 2 with CO_2/N_2 selectivity vs. CO_2

2   permeability and O_2/N_2 selectivity vs. O_2 permeability plotted. The

3   permeability was approximately 5.0 B for CO_2 and 0.75 B for O_2. The

4   selectivity of this membrane was 51 CO_2/N_2 and 6.9 for O_2/N_2. For a pure

5   PVAc membrane, CO_2/N_2 selectivity was 35 and CO_2 permeability was

6   approximately 3.1 B. Similarly, a pure PVAc membrane exhibited an O_2/N_2

7   selectivity of 5.9 and a permeability of 0.52 B.

8

9   *COMPARATIVE EXAMPLE D: PVAc-110 micro mhos/cm*

10

11   A portion of the H-SSZ-62 zeolite of Example 1 was removed when the wash

12   water conductivity was 110 micro mhos/cm, and dried, calcined, and silanated

13   as in Example 3. The zeolite was used to prepare a mixed matrix membrane

14   film with 15% zeolite loading in PVAc as in Example 3. CO_2/N_2 and O_2/N_2

15   permeation results are shown in FIGS. 1 and 2, respectively. These results

16   show lower selectivity in both cases, 44 and 6.4, than when the sieves were

17   water washed down to 30 micro mhos/cm prior to calcination.

18

19   *COMPARATIVE EXAMPLE E*

20

21   Another batch of H-SSZ-62 was prepared similar to that of Example 3, with

22   drying, calcining, and silanating after the wash water conductivity had reached

23   110 micro mhos/cm. After calcining, the zeolite was exchanged three times

24   with a 10-fold excess of an aqueous solution of NH_4NO_3 at 90°C, then

25   calcined at 400°C. This zeolite was silanated using

26   0.2% aminopropyldimethylethoxysilane (APDMES) in isopropanol/water

27   (95/5 V/V) and dried at 135°C overnight, followed by one hour at 195°C.

28   Permeation testing as in Example 3 showed an O_2 permeability of 0.68 B and

29   a O_2/N_2 selectivity of 6.3.

1   *COMPARATIVE EXAMPLE F*

2

3   A small H-SSZ-62 sample from Comparative Example E was calcined at

4   590°C for one hour. The calcined batch was silanated using 0.2% APDMES

5   in isopropanol/water (95:5 V/V) and dried at 135°C overnight. Permeation

6   testing as in Example 3 showed an O_2 permeability of 0.69 B and a O_2/N_2

7   selectivity of 6.5. For CO_2/N_2, the selectivity was 44.2.

8

9   *COMPARATIVE EXAMPLE G*

10

11   A portion of the as-synthesized zeolite of Example 3 was worked up as in that

12   example, except the zeolite was calcined at 593°C after the conductivity was

13   reduced to 110 micro mhos/cm and prior to the further water washing which

14   lowered conductivity to less than 30 micro mhos/cm. The zeolite was also

15   silanated. The zeolite was evaluated in the Mixed Matrix Membrane

16   Enhancement Test. Agglomeration of the zeolite in forming the membrane

17   contributed to no enhancement in the CO_2/CH_4 selectivity.

18

19   While in the foregoing specification this invention has been described in

20   relation to certain preferred embodiments thereof, and many details have

21   been set forth for purpose of illustration, it will be apparent to those skilled in

22   the art that the invention is susceptible to alteration and that certain other

23   details described herein can vary considerably without departing from the

24   basic principles of the invention.